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JUL 79 A D BUCK, J P BURKES

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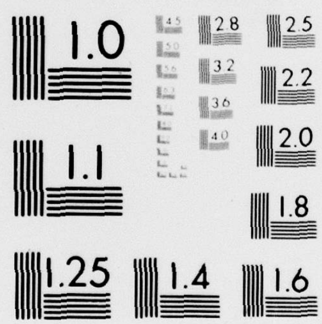

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EXAMINATION OF GROUT AND ROCK FROM DUVAL MINE, NEW MEXICO

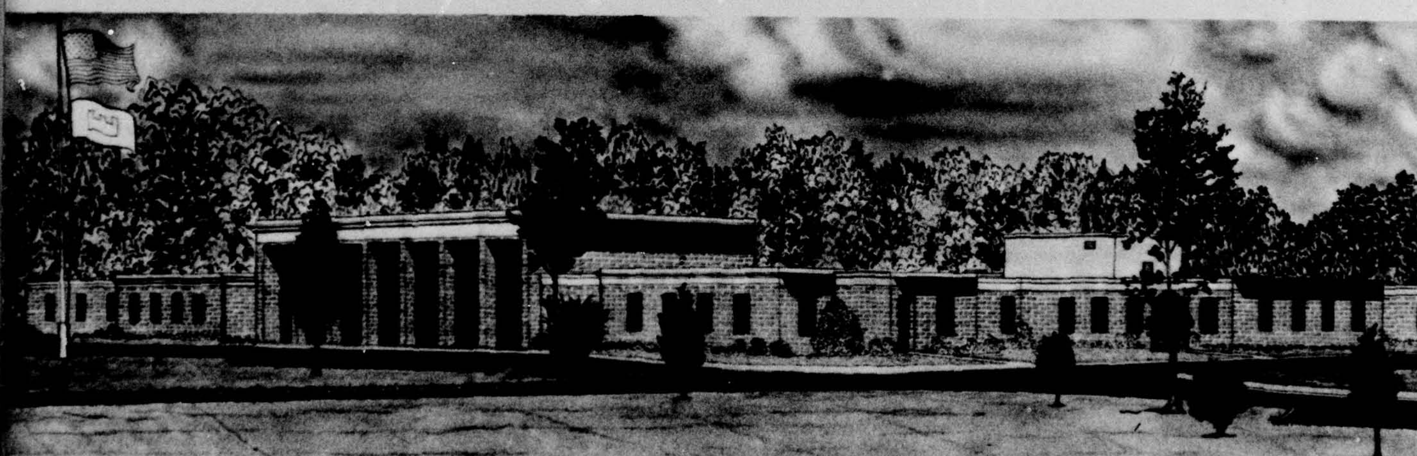
by

Alan D. Buck, Jerry P. Burkes

Structures Laboratory
U. S. Army Engineer Waterways Experiment Station
P. O. Box 631, Vicksburg, Miss. 39180

July 1979

Final Report



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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)
Petrographic examination was made of a 17-year-old grout specimen that had been surrounded by rock salt. It was found that the contact between the grout and the rock salt was tight and that the composition and microstructure of the grout seemed normal for such material. The grout contained calcium silicate hydrate, calcium hydroxide, tetracalcium aluminate dichloride-10-hydrate, and some halite and sylvite.

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PREFACE

This report covers a small part of the work involved in the Borehole Plugging Program which the U. S. Army Engineer Waterways Experiment Station (WES) is conducting for the U. S. Department of Energy.

This report was prepared by A. D. Buck and J. P. Burkes under the general supervision of B. Mather, Acting Chief, Structures Laboratory, and K. Mather, Chief, Engineering Sciences Division, Structures Laboratory.

The Commander and Director of WES during the time involved was COL J. L. Cannon, CE. Technical Director was F. R. Brown.

CONTENTS

CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI)
UNITS OF MEASUREMENT

U. S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

Multiply	By	To Obtain
cubic yards	0.7645549	cubic metres
feet	0.3048	metres
inches	25.4	millimetres
pounds (force) per square inch	6894.757	pascals

EXAMINATION OF GROUT AND ROCK FROM DUVAL MINE, NEW MEXICO

Background

1. Duval Hole D-217 in New Mexico was drilled between 17 and 20 June 1961 to a depth of 1064.5 ft.* Part of the hole was filled with a grout mixture containing 42 bags of class "C" cement, brine, and 3 percent calcium chloride ($CaCl_2$) by weight of cement. The hole was approximately 4 in. in diameter in the lower portion. The grout plug was cut by a mine tunnel at about the 1048-ft depth in October 1970. A block of rock salt and the encased grout plug was removed from this tunnel on 1 November 1978. This block had a volume of approximately 1 cu yd with the grout plug running vertically down its center. Four sections were made by horizontal cuts; each section was about 10 in. thick. Section 1 was the top section. The top surface of Section 1 was the floor of the mine tunnel.

Samples

2. Section 1 of the block described above was sent to the U. S. Army Engineer Waterways Experiment Station (WES) for tests and examination. Section 2 was sent to Pennsylvania State University, and Sections 3 and 4 were retained by Sandia Laboratories.** The petrographic examination was made to determine the composition of the 17-year-old grout and the rock and the microstructure of the interface between them in this sample. Mr. Gulick had furnished two small samples in bags of lumps of soft powdery grout and of a piece of rock about 3 by 3 in. in size. These samples had been obtained in the mine tunnel within about 10 ft of where the tunnel cut the grout plug. Since some of the material was lighter colored there was a question of whether it was rock or grout. There was also a question as to why this material was weak.

3. The latter two samples were provided by Mr. Gulick in December 1978. The "grout" was designated sample A while the "rock" was designated sample B. The dark portion of the rock was sample B-1, and the light portion was sample B-2.

4. Section 1 of the block was received at WES on 13 December 1978. A vertical core approximately 12 in. in diameter was taken through it so that the grout plug was in the center of the core. The lower inch of this core from Section 1 was sliced in kerosene with a diamond saw and used for the petrographic sample so that the sample would be as near to Section 2 as would be possible for comparison. Two samples of rock from the upper

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* A table of factors for converting U. S. cutomary units of measurement to metric (SI) units is presented on page iii.

** This information was supplied by Mr. C. W. Gulick of Sandia Laboratories.

surface of the slice from Section 1 were designated C and D for petrographic examination while the other samples from this surface were E (grout) and F (grout-rock contact). The upper surface of the slice was used because there had been less opportunity for the grout to carbonate in this fresher surface.

5. According to a USGS log of the hole, the rock in samples B-1, B-2, C, and D is from the Salado Formation of Permian Age.*

Test procedure

6. The upper surface of the slice from the bottom of Section 1 is shown in Figure 1. Samples of grout, rock, and their contact were obtained by taking small cores about 1/2 in. in diameter from this surface with a small diamond core drill. A small amount of lubricating water was used during the drilling.

7. X-ray diffraction examinations. X-ray diffraction examinations were made with an X-ray diffractometer using nickel-filtered copper radiation.

a. Grout. The grout samples were examined as tightly packed powders in a static nitrogen atmosphere using either a beaker of hot barium hydroxide solution or a sponge saturated with this solution to minimize carbonation and dehydration.

(1) Sample A. Sample A was ground and examined.

(2) Sample E. A core of sample E was vacuum-dried about 18 hr in an oven at 60°C. Part of it was then ground and examined.

b. Rock. Portions of samples B-1 and B-2 from the loose rock and core samples C and D from Section 1 were ground to pass a 45-µm (No. 325) sieve and were examined as back-packed powders to minimize preferred orientation. Samples C and D came from opposite sides of the grout plug and each was about 2 in. away from the plug. Sample C was reddish clayey rock while sample D was lighter colored rock. Portions of each of the four rock samples were dissolved in distilled water; the solution was then filtered and dried. The precipitated water-soluble material from each sample was then examined as a tightly packed powder. The water-insoluble residues of clayey samples B-1 and C were slurried onto glass slides and allowed to dry; these films were then examined air-dry, after saturation with glycerol or ethylene glycol or both (separate slides), and after heating for 1 hr at 350°C. The heated slides were examined in a static nitrogen atmosphere to prevent rehydration. The water-insoluble residue from the lighter colored rock sample B-2 was dried, ground, and examined as a back-packed powder.

c. Small slender transparent crystals were present on the surface of the light colored rock sample B-2. Some of these were hand-picked, ground in alcohol, slurried on a glass slide and examined after drying. Some of the crystals were also examined as grain immersion mounts with a polarizing microscope.

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* See footnote p 1.

8. Scanning electron microscope (SEM) examinations. Earlier experience[1] with grout samples made with salt water had suggested that freeze-drying was not removing all of the evaporable water from the grout specimens. Therefore, a modified procedure was used. The small cores of sample E (grout) and F (grout-rock interface) were vacuum dried as previously described. The dried specimens were then stored in a desiccator over silica gel. They were then freeze-dried. Fresh fracture surfaces were then made across core E and along the interface of core F. For comparison another vacuum-dried core sample of E and of F were fractured without freeze-drying. In each case the fresh fracture surface was coated with about 5 nm of carbon followed by about 15 nm of 80/20 gold-palladium alloy in a vacuum evaporator. Both sides of the fractured interface contact of F cores were examined. All SEM examinations were made using an Advanced Metals Research No. 900 unit.

Results

9. Preliminary inspection of the entire Section 1 block of rock salt and included grout plug and of the petrographic sample sawed from the bottom of Section 1 indicated the following features:

a. The contact between the grout and the rock was tight everywhere that it could be seen. This tight contact is well shown in Figure 1. The interface in the F samples had to be separated using pliers which also indicates the tightness of the contact.

b. The appearance of the rock salt in Section 1 ranged from purer and lighter colored salt to a reddish more impure clayey salt. The petrographic samples (C, D) were selected to exemplify this range of compositions. The same sort of range was present in hand samples B-1 and B-2.

10. Rock. The rock of Section 1 as typified by samples C and D and subsamples B-1 and B-2 of hand sample B ranged from pure or almost pure halite to a complex assemblage of other minerals including sylvite, langbeinite, brugnatellite, loeweite, kainite, brucite, gypsum, calcite, magnesite, talc, quartz, and clay minerals. Most of the minor nonclay minerals are hydrous sulfates or chlorides or both along with some carbonates. The clay minerals included a regularly interlayered mixed-layer clay, smectite,* chlorite, kaolinite, and clay-mica.** The mixed-layer clay was thought to be chlorite-smectite because there was some peak shifting associated with the addition of glycerol or ethylene glycol. The compositions of these samples are shown in Table 1. They are generally similar to Duval Mine wall rock samples as shown in Table 7.9 of the WIPP report.[2] The main difference is that no polyhalite was found in samples B-1, B-2, C, and D.

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* Swelling clay; the montmorillonite-saponite group.

** Illite or clay-sized mica or both; characterized by a 10-Å (1.0 nanometre) spacing.

11. The crystals found on the surface of rock sample B-2 were halite and sylvite. Sample B-2 was an impure salt (Table 1). The crystals on the surface of sample B-2 resembled similar crystals found on ERDA 10 grout samples;[1] this tended to confirm the conclusion that the samples on the ERDA 10 grout were salt whiskers produced by incomplete removal of water by freeze-drying before SEM examination.

12. <u>Grout</u>. The compositions of samples A and E were similar. Both contained calcium silicate hydrate (CSH), calcium hydroxide, and tetracalcium aluminate dichloride-10-hydrate ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot H_2O$) (chloroaluminate) along with some halite and sylvite. The chloroaluminate was probably the beta form. Sample A also contained a small amount of ettringite which was absent from sample E. There were no detectable phases of unhydrated portland cement.

13. The reason the sample A grout was less intact than the sample E grout was probably that it contained more water and was thus weaker, or that it had been disrupted and abraded during construction of the mine tunnel, or possibly both.

14. Eight scanning electron micrographs of the grout are shown in Figures 2-5. The pair in Figure 2 show the grout side of the grout to rock contact (sample F) at two magnifications. While it is not shown, the rock side was similar but showed more salt, as would be expected, than the grout side. Figures 3 and 4 show grout sample E at two magnifications. They also show that the effect of freeze drying after lengthy vacuum drying was not significant. These four photomicrographs show the typical microstructure of this grout. This open microstructure, when compared with the microstructure of other cement pastes of known low water-cement ratio, is proof that the Duval sample had a high water content. This comparison was illustrated by SEM photomicrographs in the ERDA 10 report.[1] The low unconfined compressive strength of about 300 psi for the Duval Mine grout verifies what is indicated by the open structure in Figures 3 and 4.

15. Figure 5 is an enlargement of part of the upper sample shown in Figure 4. It shows what are believed to be upright films of salt deposited as water is removed during sample preparation. The results of this and the ERDA 10 work[1] strongly suggest that the removal of moisture from a grout containing soluble salts by freeze drying or by lengthy vacuum drying with or without subsequent freeze drying, results in efflorescent salt deposits on sample surfaces.

16. Figure 6 is another SEM view of grout sample E. It shows massive calcium hydroxide and a feature illustrating encapsulation.

Discussion

17. Comparison of X-ray diffraction patterns and SEM photomicrographs of the present 17-year-old grout with those of the ERDA 10 grout at

ages of approximately 2 weeks[1] and 1 year show general similarities in composition and microstructure. Specific comments are given below:

a. The grouts are characterized by the presence of CSH, calcium hydroxide, chloroaluminate, and salt.

b. The development seems to be that ettringite is present at earlier ages and is partly or totally replaced by the chloroaluminate with the passage of time.

c. There is unhydrated calcium aluminoferrite in the ERDA 10 samples but not in the Duval samples. This should mean that this cement compound hydrated with time and is absent in the 17-year-old grout. It is quite possible that complete hydration was achieved within 1 month. This complete hydration of the cement is another indication of high water content as is the open structure.

d. There is a more pronounced CSH peak at 0.3^{+} nm with these grouts than with portland cement pastes made with fresh water. This suggests better crystallinity of the CSH in the saltwater grouts.

18. Since the 17-year-old Duval Mine grout is much like the ERDA 10 grouts this indicates satisfactory stability for these combinations of materials in a salt environment at slightly elevated temperatures for the time span covered.

19. The bond of grout to salt was visually intact and physically strong for the Duval Mine sample.

20. A lower water content would be preferable, because it would lead to a more impermeable grout.

21. Examination of hand samples of loose grout and rock from the area where Section 1 was taken indicated the grout was similar in composition to the grout plug in Section 1 and none of the white material was grout.

References

1. U. S. Army Engineer Waterways Experiment Station Petrographic Report, "Examination of Grout Samples for Project ERDA 10," 4 Jan 1978.

2. Powers, D. W., Lambert, S. J., Shaffer, Sue-Ellen, Hill, L. R., Weart, W. D., editors, "Geologic Characterization Report, Waste Isolation Pilot Plant (WIPP) Site, SE New Mexico," Vol 2, Sandia Laboratories, Dec 1978, Albuquerque, N. Mex., and Livermore, Calif.

Table 1

Mineralogical Composition of Four Rock Salt Samples by X-Ray Diffraction

Constituents	Hand Samples B-1	Hand Samples B-2	Section 1 Sample C	Section 1 Sample D
Nonclays				
Halite*	X**	X	X	X
Sylvite	–	X	?	–
Langebeinite	X	–	X	–
Brugnatellite	?†	X	–	–
Loeweite	–	–	X	–
Kainite	–	–	X	–
Brucite	?	X	–	–
Gypsum	?	X	–	–
Calcite	–	X	–	–
Magnesite	X	–	X	–
Talc	X	X	X	–
Quartz	–	?	–	–
Clays				
Regularly interstratified mixed-layer type††	X	–	X	–
Smectite (monovalent)	–	?	–	–
Chlorite	X	–	X	–
Clay-mica	X	–	X	–
Kaolinite	?	–	X	–

* Major component of all four samples.
** Indicates the material is present.
† May be present.
†† Probably chlorite-smectite.

Figure 1. Central portion of sawed surface from lower part of Section 1, X0.8. The circular area is the grout plug surrounded by rock salt. Note the uniformly tight contact of grout and rock salt.

Figure 2. Samples X230 (top) and X2300 (bottom) of grout side of grout to rock salt contact from Section 1 (Sample F), Duval Mine. X2300 is an enlargement of the midportion of X230; it is believed to show CSH, calcium hydroxide, possibly monochloroaluminate, and evaporated salt.

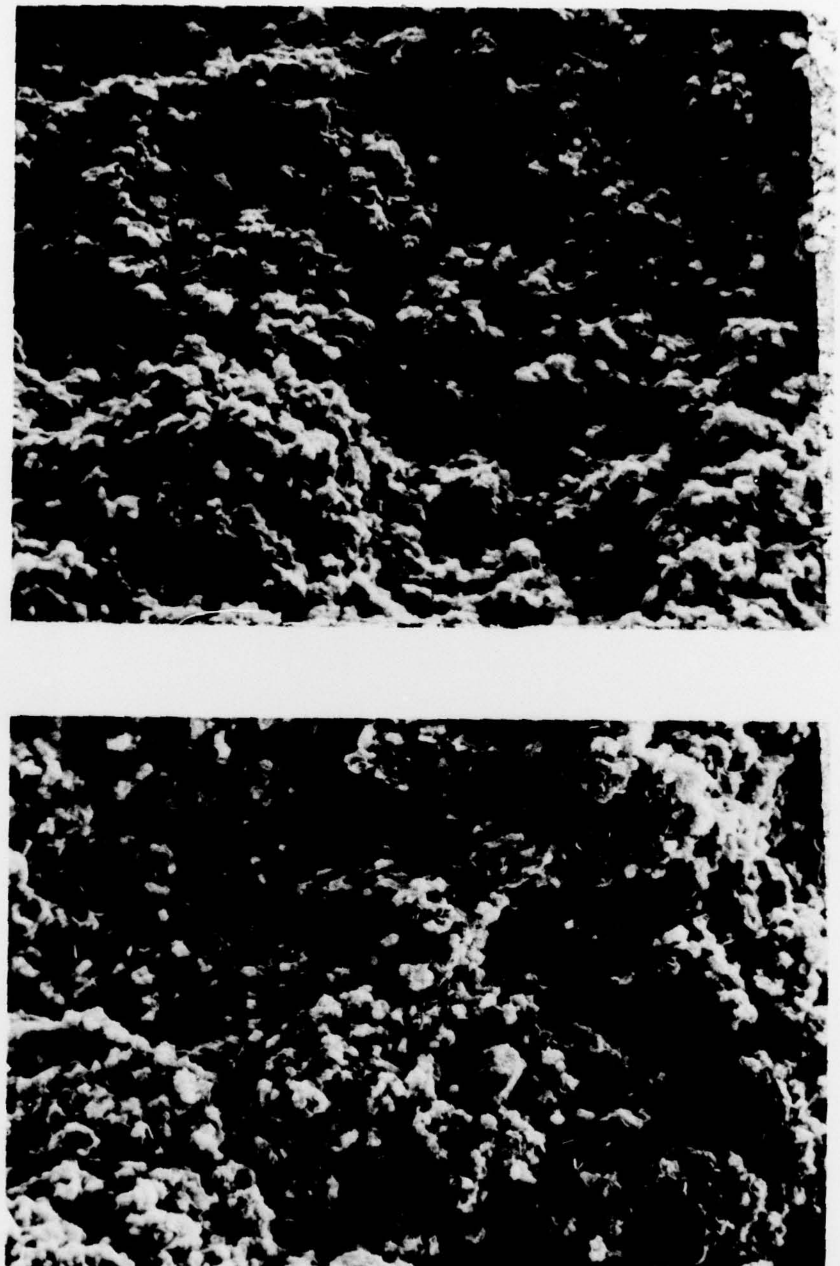

Figure 3. Grout samples E, X230. Both were vacuum dried before coating. The upper sample was then freeze dried while the lower one was not. There is no detectable difference in the two samples.

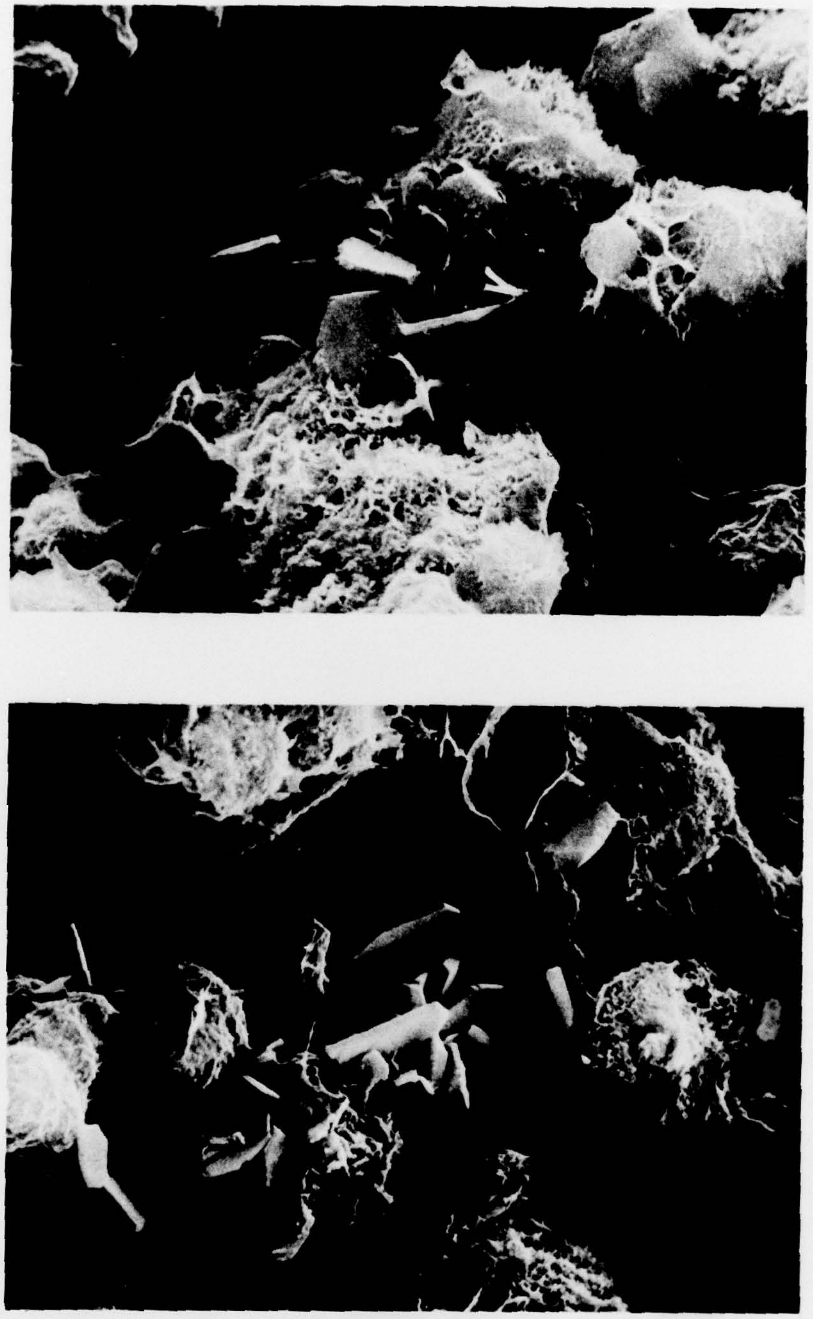

Figure 4. Grout samples E, X2300. Upper sample was freeze dried following vacuum drying while bottom one was not. There is no detectable effect of this difference. These are enlargements of the areas shown in Figure 3.

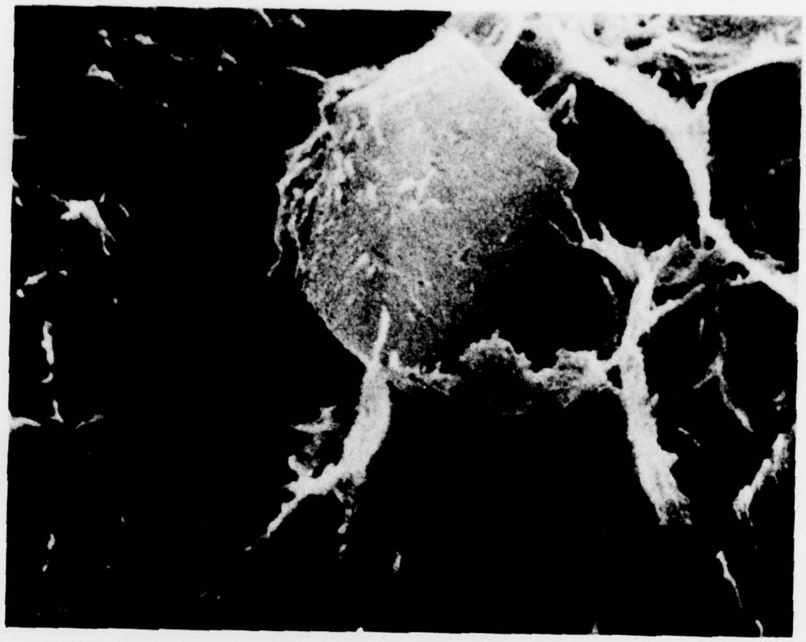

Figure 5. Grout sample E, X11,500. This is an enlargement of upper right of top sample in Figure 4. The thin upright films are believed to be salt (halite, sylvite) that precipitated as moisture evaporated during specimen preparation.

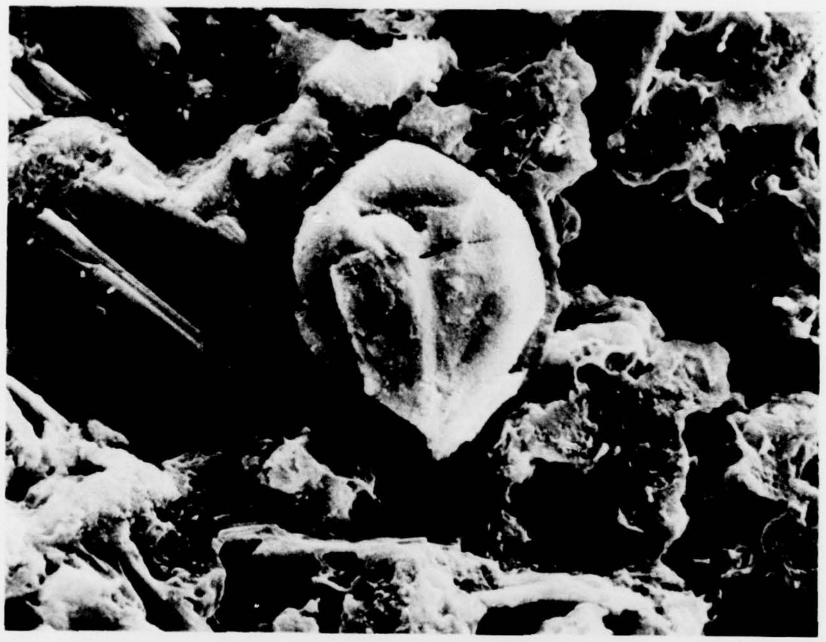

Figure 6. Grout sample E, X1150. Massive calcium hydroxide is visible in upper left and left center. The main feature of interest is the large encapsulated grain in the center of the field. This may be calcium hydroxide (CH) or CH and CSH replacing an original cement grain.

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